Flammability Characteristics of Methylacetylene, Propadiene (Allene), and Propylene Mixtures

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An investigation was conducted to determine the flammability characteristics of potentially hazardous mixtures containing methylacetylene, propadiene, and hydrocarbon diluent, such as propylene or propane. A 38-gage platinum fuse wire was used as the ignition energy source. The range of flammable mixtures at an initial temperature of 120° C. was greatest with high concentrations of propadiene and increased with an increase in pressure and vessel diameter ($\geqq 12$ inches). Lower explosion pressure limits were about 16 p.s.i.g. for propadiene and 39 p.s.i.g. for methylacetylene. The rates of pressure development and amounts of carbon, hydrogen, and methane formed varied consistently with the initial pressure and/or vessel diameter.

METHYLACETYLENE and propadiene, which are commercially available, are potentially hazardous because their vapors can decompose exothermally and propagate flame in the absence of oxygen. Heat from surroundings may be sufficient to effect their decomposition and ignition. With increasing temperature and pressure their thermal stability may be expected to decrease. The present investigation was conducted to determine the flammability characteristics of gas or liquefied gas mixtures containing these materials together with a hydrocarbon diluent, such as propylene or propane. Flammable mixtures are defined here as those capable of propagating flame when ignited by an external energy source, such as a platinum fuse wire.

The fundamental properties of the methylacetylene decomposition flame at elevated pressures have been studied recently. Hall and Straker (*4*) report that its burning velocity is about 2 cm./sec. between 10 and 40 atmospheres—a relatively low value in comparison to most known flames. They report a critical pressure for flame propagation of 43 p.s.i.g. (lower pressure limit) at about 20° C., in a 4-inch-diameter tube. This may be compared with the critical pressure limit of 50 p.s.i.g., in a 2-inch-diameter tube, reported by Fitzgerald (*2*). Methylacetylene is more stable than acetylene which also forms a decomposition flame. The low pressure limit of acetylene in a 2-inch tube is only about 6 p.s.i.g. (*7*). Although little information is available on the stability of propadiene, recent experiments indicate that the energy requirements for the ignition of propadiene-methylacetylene mixtures are comparable to those required for the ignition of methylacetylene alone (*8*).

Like acetylene, methylacetylene and propadiene can be stabilized in a system at a specified temperature and pressure by the adding of inert gases or hydrocarbons that do not decompose under the given conditions. Fitzgerald (*2*) reports ethane to be a much better stabilizer than either methane or nitrogen. In the present study, the use of propylene and propane as diluents is examined because of the current interest in these hydrocarbons as stabilizers for methylacetylene and for methylacetylene-propadiene mixtures. The flammability characteristics of such mixtures (vapor) are shown to be sensitive to temperature and pressure, as well as to the size of the reaction chamber.

EXPERIMENTAL APPARATUS AND PROCEDURE

Limit of Flammability Measurements. Flammability limits of the methylacetylene-propadiene-propylene system were determined at elevated temperatures and pressures in cylindrical stainless steel bombs measuring 1, 2, 4, and 12 inches in diameter, respectively, and in a spherical bomb of 24-inch diameter. The cylinders were about 42 inches long, except for the 12-inch diameter one which was 17 inches long. All of the bombs were insulated with asbestos and heated externally with Nichrome ribbon elements (see Figure 1). Chromel-Alumel thermocouples (22-gage), located near the top and bottom of each bomb, were used to follow the heating of the test mixtures introduced into the vessesl; thermocouple outputs were measured by a potentiometer. The partial pressure of each mixture component was measured by a mercury manometer or by a Bourdon gage which also served to indicate if ignition occurred. A continuous pressure record was obtained during each experiment with an SLM Kistler transducer system whose output was fed to an oscilloscope equipped with a camera. In most determinations, the ignition source consisted of about one inch of 38-gage platinum wire located at the bottom of the test vessel.

In preparing for an experiment, a vapor mixture from the liquefied gases were made up in an explosion bomb which had previously been evacuated. To facilitate transfer of the gases from their supply cylinders, the latter were immersed in a water bath maintained at a selected temperature between 20° and 45° C.; the explosion bomb was kept at the same temperature. Generally, at least one of the gases was introduced in two increments and alternately with the other gas or gases. To effect mixing, a thermal gradient of about 60° C. was maintained for at least one hour between the top and bottom of the bomb. Calculated mixture compositions, corrected for compressibility, were in close agreement with mass spectrometric analyses made for a few sample mixtures.

After the gases were mixed, the bomb was heated to the desired temperature and the platinum wire was fused. Ignition and extent of flame propagation were determined from the pressure measurements and from the amount of carbon formed. In some instances, complete analyses of the cooled product gases were made. Most of the experiments were performed at 120° C. and at pressures of 50 and 100 p.s.i.g.

The methylacetylene used in this work had a minimum purity of 95 per cent and could contain as much as 4 per cent nitrogen according to the vendor's specifications; mass spectrometer analysis of our sample showed about 2 per cent nitrogen present. The propadiene and proylene were about 97.5- and 99-per cent pure, respectively; propylene was the main impurity in the propadiene.

RESULTS AND DISCUSSION

Flammability Limits of the Methylacetylene-Propadiene-Propylene System. Mixtures of methylacetylene and propadiene vapors, which were ignited with a 1-inch length of 38-gage platinum fuse wire, were found to be flammable (in the absence of air) in all proportions at the initial conditions of 120° C. and 50 p.s.i.g. Addition of propylene to either of these components produced limit mixture compositions which were dependent upon the temperature and pressure as well as on the vessel diameter. Limit compositions found at 120° C. and at 50 or 100 p.s.i.g. are given in Table I for vessel diameters of 1 to 24 inches. The data in Table I were used to make up the ternary diagram shown in Figure 2. This figure shows the approximate range of flammable mixtures for the methylacetylene–propadiene–propylene system under the experimental conditions noted. In any given vessel, the range of flammable mixture compositions is greatest with high concentrations of propadiene. For example, propadiene–propylene mixtures containing up to 31.3 per cent propylene are flammable in the 12-inch-diameter bomb at 100 p.s.i.g.; 21.9 per cent is the limiting propylene concentration for methylacetylene–propylene mixtures.

The propadiene used in this investigation propagated flame when ignited by the platinum fuse wire at pressures in excess of 16 p.s.i.g. at 120° C. in a 2-inch-diameter bomb; the methylacetylene required pressures greater than 39 p.s.i.g. Other investigators have reported similar pressure limits of 31 p.s.i.g. at 120° C. and about 45 p.s.i.g. at 150° C. for methylacetylene in 2-inch and 1¼-inch-diameter bombs, respectively (*2*, *8*).

It is not altogether surprising that methylacetylene should be more stable than propadiene because the former contains a methyl group that provides increased resistance to thermal degradation. Pyrolysis experiments by Meinert and Hurd (*9*) indicate the same order of stability for these liquefied gases when heated to temperatures between 400° and 650° C. They also obtained evidence that methylacetylene first converts to propadiene, which then polymerizes and eventually decomposes.

The flammable range of the mixtures was noticeably greater in the experiments conducted at 100 p.s.i.g. than at 50 p.s.i.g. (Figure 2). In view of the lower explosion pressure limits given above for methylacetylene and propadiene, it was to be expected that the flammability of the mixtures would be pressure sensitive under the experimental conditions; even propylene will propagate flame at sufficiently high temperatures and pressures. It was also to be expected that an increase in temperature would widen the limits of flame propagation. In some preliminary experiments at 60° C. and 50 p.s.i.g., mixtures of methylacetylene and propylene failed to ignite in the 2-inch-diameter bomb with the ignition source used (1 inch of 38-gage platinum wire). these mixtures ignited readily at 120° C. and 50 p.s.i.g. in the same bomb. It is possible that with other ignition sources, these mixtures would ignite and propagate flame at the lower temperature (60° C.) since ignition energy requirements become most critical near the limiting pressure conditions for flame propagation.

The effects of initial pressure, vessel diameter, and mixture composition were also reflected in the pressure measurements. Pressure-time records from experiments in the 1-, 2-, and 4-inch-diameter bombs with near-limit mixtures of propadiene–propylene and methylacetylene–propylene are shown in Figure 3 (A and B); pertinent data from these records are given in Table II. The rates of pressure rise and the maximum explosion pressures de-

Table I. Flammability Limits of Methylacetylene–Propylene–Propadiene Mixtures at 120° C. in Various Sized Vessels[a]

Initial Press., P.S.I.G.	Methylacetylene, Vol. %	Propylene, Vol. %	Propadiene, Vol. %
	1-inch ID Bomb (0.47 liter)		
100	92.8	7.2	...
100	...	19.8	80.2
	2-inch ID Bomb (2.03 liters)		
50	94.7	5.3	...
50	...	15.3	84.7
100	90.4	9.6	...
100	...	23.8	76.2
100	39.4	21.5	39.1
	4-inch ID Bomb (7.86 liters)		
100	84.5	15.5	...
100	...	28.7	71.3
	12-inch ID Bomb (31.0 liters)		
100	78.1	21.9	...
100	...	31.3	68.7
	24-inch ID Bomb (118.7 liters)		
100	>76	<24	...
100	...	32.5	67.5

[a] Ignition source consisted of one inch of 38-gage platinum fuse wire.

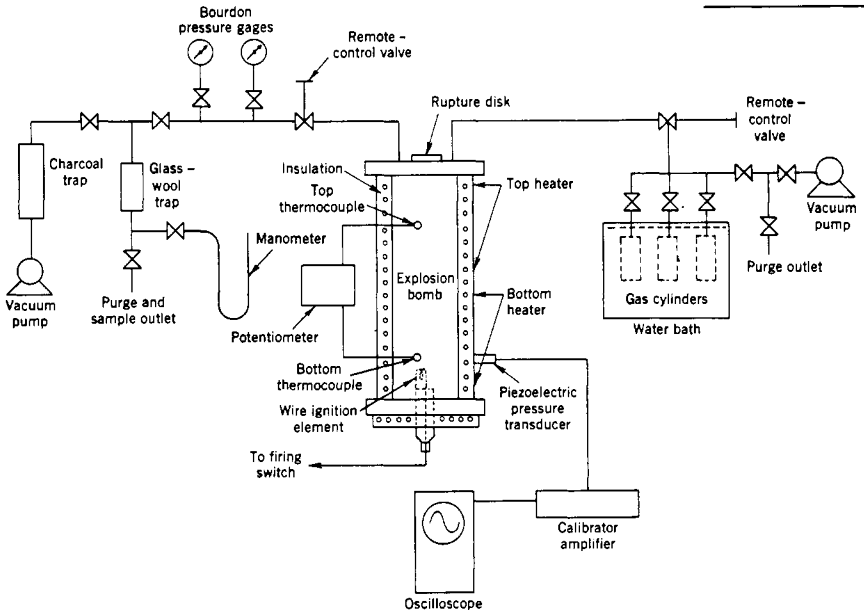

Figure 1. Experimental setup for flammability determinations

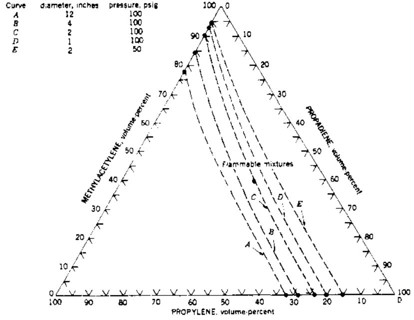

Figure 2. Range of flammable mixtures for the methylacetylene–propadiene–propylene system at 120° C. and at 50 and 100 p.s.i.g.

veloped decrease markedly with a decrease in bomb diameter. For example, the initial rates of pressure rise for the propadiene–propylene mixtures were 60 and 250 p.s.i./sec. in 1- and 4-inch-diameter bombs, respectively; the corresponding ratios of maximum explosion pressure to initial pressure were 2.15 and 5.82. Comparable data were obtained with methylacetylene–propylene mixtures. It was evident from these and other results that the heat losses were greatest for the smallest vessel. The quenching diameter for methylacetylene flames is reported to be less than 0.3 cm. at initial mixture conditions of 15 p.s.i.a. and 120° C. (*4*); with propylene as diluent, the quenching diameter should be greater under the same conditions.

Explosion pressure-time histories for the flammability determinations conducted in the 2-inch-diameter bomb with propadiene and methylacetylene at various initial pressures are also shown in Figure 3 (C and D). Maximum explosion pressures were attained more rapidly with propadiene than with methylacetylene, at a given initial pressure. At the explosion pressure limit for propadiene (16 p.s.i.g.), the initial and maximum rates of pressure rise were only 25 and 55 p.s.i./sec., respectively (Table III). These rates, and those obtained for mixtures of these gases with propylene, increased noticeably as the initial pressure and the diameter of the vessel were increased. Because of the relatively low rates of pressure rise observed in most of these determinations, the times required to reach a given pressure were long, as compared to those that are generally observed with combustible-oxidant mixtures in similar bombs. As noted in Table II, the times required to attain maximum pressures were greater than 1 second except in experiments conducted in the 4-inch-diameter bomb; these data indicate the slow development and propagation of flame that can be expected in the decomposition of these materials.

The effect of vessel size on the flammability limits of methylacetylene-propylene and propadiene–propylene mixtures at the initial conditions of 120° C. and 100 p.s.i.g. is illustrated in Figure 4. The concentration of diluent (propylene) required to produce limit mixtures increased with an increase in vessel diameter from 1 to 12 inches; above 12 inches the diamter had little effect. The following equations were found to fit the experimental data by the method of least squares for the range of vessel diameters, *d*, indicated:

Methylacetylene–propylene mixtures:

$$\text{Vol. \% propylene} = 4.1 + 3.2d - 0.14d^2;\ 1'' \leq d \leq 12'' \tag{1}$$

Propadiene–propylene mixtures:

$$\text{Vol. \% propylene} = 18.3 + 3.0d - 0.16d^2;\ 1'' \leq d \leq 12'' \tag{2}$$

The volume per cent of propylene is the amount required to obtain a limit mixture.

The vessel-diameter effect observed for these mixtures can be attributed largely to the slow flame propagation obtained with these materials. During most of the burning period, the burning velocities probably did not exceed about 2 cm./sec., the value reported by Hall and Straker (*4*) for pure methylacetylene at 10 atmospheres. With such a low burning velocity, the total heat losses to the walls by conduction and radiation can be significant enough to cause flame extinction. It is to be expected that such effects would be most evident, as is the case here, for the smallest diameter vessels or those with the greatest contact area-to-volume ratio. If judged by the burning velocities and flame temperatures, heat losses due to radiation appear to be very important in the propagation of decomposition flames through methylacetylene and acetylene; observed flame temperatures are much less than values calculated assuming no radiation losses (*1*, *3*). However, it has not been established whether such heat losses alone determine the explosion pressure limits of these flames.

The main (cooled) decomposition products from the ignition of methylacetylene and propadiene were found to be carbon, hydrogen, and methane (Table III); small or trace quantities of ethane, ethylene, and unreacted gas were also present. Similar results have been obtained with methylacetylene and with acetylene by other investigators (*1*, *2*). However, acetylene generally undergoes more complete decomposition to the elements, (carbon and hydrogen) when ignited by an external energy source

Table II. Pressure Data from Flammability Experiments with Methylacetylene–Propylene–Propadiene Mixtures at 120° C., and at Various Pressures

Propylene, Vol. %	Bomb Diameter, Inches	Initial Pressure, P_1, P.S.I.G.	Maximum Pressure, P_2, P.S.I.G.	Pressure Ratio, P_2/P_1, P.S.I.A./P.S.I.A.	Time to Maximum Pressure,[a] Sec.	Initial Rate of Pressure Rise, P.S.I./Sec.	Maximum Rate of Pressure Rise, P.S.I./Sec.
			Methylacetylene				
None	2	45	233	4.18	1.295	70	320
None	2	100	610	5.46	1.190	160	1060
			Propadiene				
None	2	16.5	68	2.67	2.070	25	55
None	2	18.5	89	3.17	1.335	35	115
None	2	22	226	6.62	1.240	65	440
None	2	100	600	5.37	1.020	150	1180
			Methylacetylene + Propylene				
6.9	1	82	173	1.95	2.020	50	60
5.0	2	50	289	4.71	1.330	90	470
7.9	2	90	458	4.53	1.310	115	630
15.0	4	100	690	6.24	0.790	270	1510
			Propadiene + Propylene				
19.3	1	100	231	2.15	1.830	60	100
21.5	2	100	304[b]	2.79[b]	0.945[b]	160	430[b]
27.9	4	100	652	5.82	0.810	250	1490
			Methylacetylene (40.1%) + Propadiene (39.7%) + Propylene (20.2%)				
20.2	2	100	419[b]	3.78[b]	1.195[b]	145	810[b]

[a] Times measured from point of initial pressure rise. [b] Maximum pressures were not observed.

Table III. Decomposition Products in Flammability Experiments with Methylacetylene–Propylene-Propadiene Mixtures at 120° C. and at Various Pressures

Initial Propylene Content, Vol., %	Bomb Diameter, Inches	Initial Pressure, P.S.I.G.	Carbon Formed, Grams	Gaseous Products (Vol. %) Hydrogen	Methane	Ethane	Ethylene	Nitrogen and carbon monoxide	Unreacted gas	Hydrogen-Carbon Mole Ratio Input	Output	Carbon Conversion,[a] %
					Methylacetylene							
None	2	42	6.61	71.0	25.4	0.3	0.2	1.8	1.3	1.33	1.44	71
Do.	2	45	6.92	...	...	...	...	...	...	...	...	71
Do.	2	60	9.19	...	...	...	...	...	...	...	...	74
Do.	2	100	13.89	73.4	19.0	0.1	0.1	1.8	5.6	1.33	1.48	73
					Propadiene							
None	2	16.5	2.89	61.5	29.8	0.6	2.3	0.7[b]	5.1	1.33	1.36	58
Do.	2	18.5	3.48	...	...	...	...	...	...	...	...	67
Do.	2	50	7.65	72.7	20.9	0.3	0.3	2.3	3.5	1.33	1.40	74
Do.	2	100	15.69	81.7	16.3	0.1	0.1	...	1.8	1.33	1.42	82
					Methylacetylene + Propylene							
6.9	1	82	1.52	...	...	...	...	...	...	...	...	40
7.9	2	90	12.28	...	...	...	...	...	...	...	...	70
15.0	4	100	60.68	79.1	18.2	...	...	1.7	1.0	1.43	1.75	82
					Propadiene + Propylene							
19.3	1	100	1.80	...	...	...	...	...	...	...	...	42
23.3	2	100	13.90	...	...	...	...	...	...	...	...	75
27.9	4	100	56.81	...	...	...	...	...	...	...	...	80
					Methylacetylene (50%) + Propadiene (50%)							
None	2	50	7.58	...	...	...	...	...	...	...	...	74
					Methylacetylene (40.1%) + Propadiene (39.7%) + Propylene (20.2%)							
20.2	2	100	13.55	...	...	...	...	...	...	...	...	74

[a] Mole-per cent of available carbon converted to free carbon. [b] Benzene.

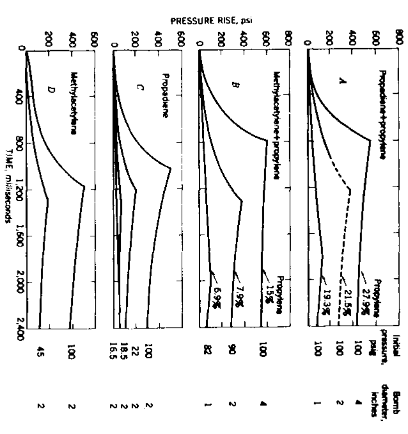

Figure 3. Pressure-time records following the ignition of methylacetylene, propadiene, and propylene mixtures at 120° C. and various initial pressures

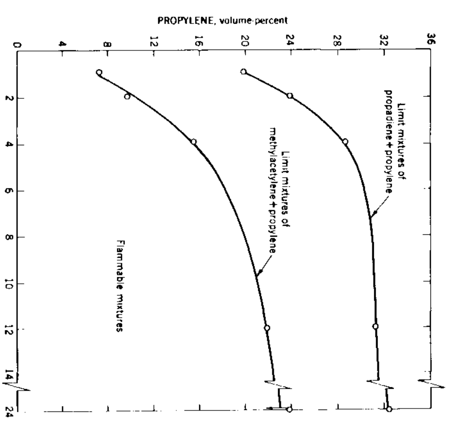

Figure 4. Effect of vessel diameter on limits of flammability of methylacetylene–propylene and propadiene–propylene mixtures at 120° C. and 100 p.s.i.g.

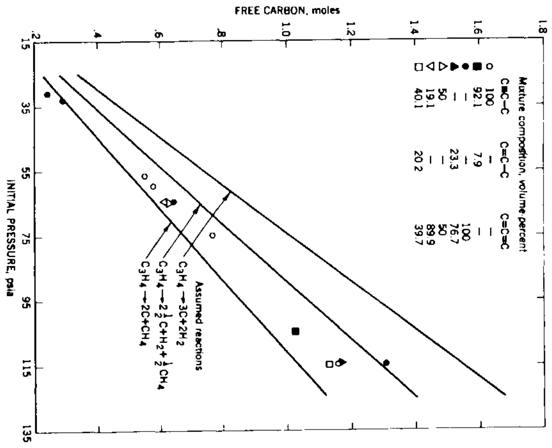

Figure 5. Free carbon formed in explosive decomposition of methylacetylene, propadiene, and propylene mixtures at 120° C. and various initial pressures (2-inch-diameter bomb)

(such as a platinum fuse wire) at the temperatures and pressures employed here. Hydrogen production increased with an increase in initial pressure, whereas the methane content decreased. Ethane and ethylene were barely detectable in the products formed at the maximum mixture pressure (100 p.s.i.g.), but they were present in significant amounts (0.6 per cent ethane and 2.3 per cent ethylene) in the experiment with propadiene at a pressure of 16.5 p.s.i.g.; benzene (0.7 per cent) was also found at this low initial pressure. The same gases form as products of the explosive decomposition of ethylene at elevated temperatures and pressures (*10*). Hurd and Meinert also report similar products from the pyrolysis of propylene between 600° and 955° C. (*6*). however, they did not find any evidence of aromatic hydrocarbons in the pyrolysis of methylacetylene or propadiene between 400° and 650° C. (*9*). A mechanism by which these C_3-unsaturated hydrocarbons may pyrolyze to form benzene through dimerization of C_3-fragmentary intermediates has been described recently by Hurd and coworkers (*5*).

Figure 5 shows that the amount of free carbon formed was nearly insensitive to mixture composition and increased linearly with initial pressure; these data were obtained in the flammability experiments at 120° C. in the 2-inch-diameter bomb. The experimental carbon yield is compared to that which would be expected from the assumed reactions that identify the three curves given in this figures. It is seen that the experimental data fall essentially between the bottom and middle curves which correspond to carbon yields of 2 and 2.5 moles, respectively, per mole of methylacetylene ($HC{\equiv}C{-}CH_3$) or propadiene ($H_2C{=}C{=}CH_2$). However, the gas compositions of the cooled combustion products were not altogether consistent with those of the reactions assumed here.

Material balances based on the complete analyses of the combustion products from methylacetylene and propadiene are given in Table IV. As the decomposition products were largely carbon, hydrogen and methane, small quantities of ethane, ethylene, etc., were neglected.

Best material balances were obtained at the initial mixture pressure of 100 p.s.i.g.; essentially, only small amounts of additional carbon are needed to obtain agreement between the input and output materials at this pressure. The mole ratio of total hydrogen to carbon was 1.33 for both reactants; it was between 1.36 and 1.48 for their reaction products, including minor constituents such as ethane, ethylene, etc. (Table III). The apparent shortage of carbon may be ascribed to the fact that all of the carbon formed in the reaction vessel was not removed and weighed. The amount of hydrogen adsorbed in the carbon probably did not introduce a serious error, however, the adsorption of significant amounts of complex condensables which may have formed would be expected to alter the material balances given here.

The combustion products from an ignition in the 4-inch diameter bomb with 85 per cent methylacetylene and 15 per cent propylene at 100 p.s.i.g. and 120° C. were also analyzed (Table III). The products were again chiefly carbon, hydrogen, and methane, and the material balance was much like that observed with methylacetylene or propadiene alone (Table IV).

The ability of paraffin hydrocarbon diluents to stabilize liquefied gases appears to depend partly upon the heat of formation of the diluent. For example, the stability of methylacetylene (*2*) and acetylene (*7*) increases with the addition of paraffins of increased molecular weight and decreased heat of formation (negative). The effectiveness of these diluents and of nitrogen decreased in the following order:

Butane > propane > ethane > methane > nitrogen

Thus, butane and propane should be preferred as stabilizers for these liquefied gases; they should also be favored over propylene which has a positive heat of formation. The ability of the diluents to absorb heat can also be an important factor here and probably accounts to a large extent for the greater effectiveness observed with hydrocarbons than with nitrogen.

CONCLUSIONS

Mixtures of methylacetylene and propadiene vapors are flammable in all proportions when ignited with a 1-inch length of 38-gage platinum fuse wire at an initial mixture temperature of 120° C. and a pressure of 50 p.s.i.g. Nonflammable mixtures are formed by adding propylene and are dependent on such variables as temperature, pressure, vessel diameter, and ignition energy. The range of flammable mixtures increases when the initial pressure is increased from 50 to 100 p.s.i.g. It increases also when the diameter of the reaction vessel is increased from 1 to 12 inches; above 12 inches the diameter has little effect.

The low pressure (explosion) limits are about 16 p.s.i.g. for propadiene, and 39 p.s.i.g. for methylacetylene at 120° C. in a 2-inch-diameter bomb. Initial rates of pressure rise following ignition of the test materials are very low and are indicative of unusually low burning velocities. These rates increase with an increase in vessel diameter and pressure.

The end products formed by explosive decomposition of methylacetylene between 42 and 100 p.s.i.g. and of propadiene between 16 and 100 p.s.i.g. are chiefly carbon, hydrogen, and methane; methylacetylene–propylene mixtures give similar products. An increase in pressure increases the percentage of hydrogen and decreases the percentage of methane. Decomposition of these liquiefied gases to their elements was less complete than that of acetylene at the same conditions.

Table IV. Material Balances for the Explosive Decomposition of Methyl-Acetylene, Propadiene, and Methylacetylene-Propylene Mixtures at 120° C., and Various Initial Pressures

Initial Pressure, P.S.I.G.	Bomb Diameter, Inches	Reactants (Moles)[a]	Carbon, Moles	Hydrogen, Moles	Methane, Moles
42	2	$(1)HC{\equiv}C{-}CH_3$	2.16	1.08	0.39
100	2	$(1)HC{\equiv}C{-}CH_3$	2.34	1.34	0.35
16.5	2	$(1)H_2C{=}C{=}CH_2$	1.86	0.75	0.36
50	2	$(1)H_2C{=}C{=}CH_2$	2.36	1.19	0.34
100	2	$(1)H_2C{=}C{=}CH_2$	2.54	1.44	0.29
100	4	$(1)HC{\equiv}C{-}CH_3{}^{+}$ $(0.175)H_2C{=}CH{-}CH_3$	2.96	2.00	0.46

[a] Numbers in parentheses indicate moles of reactant.

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